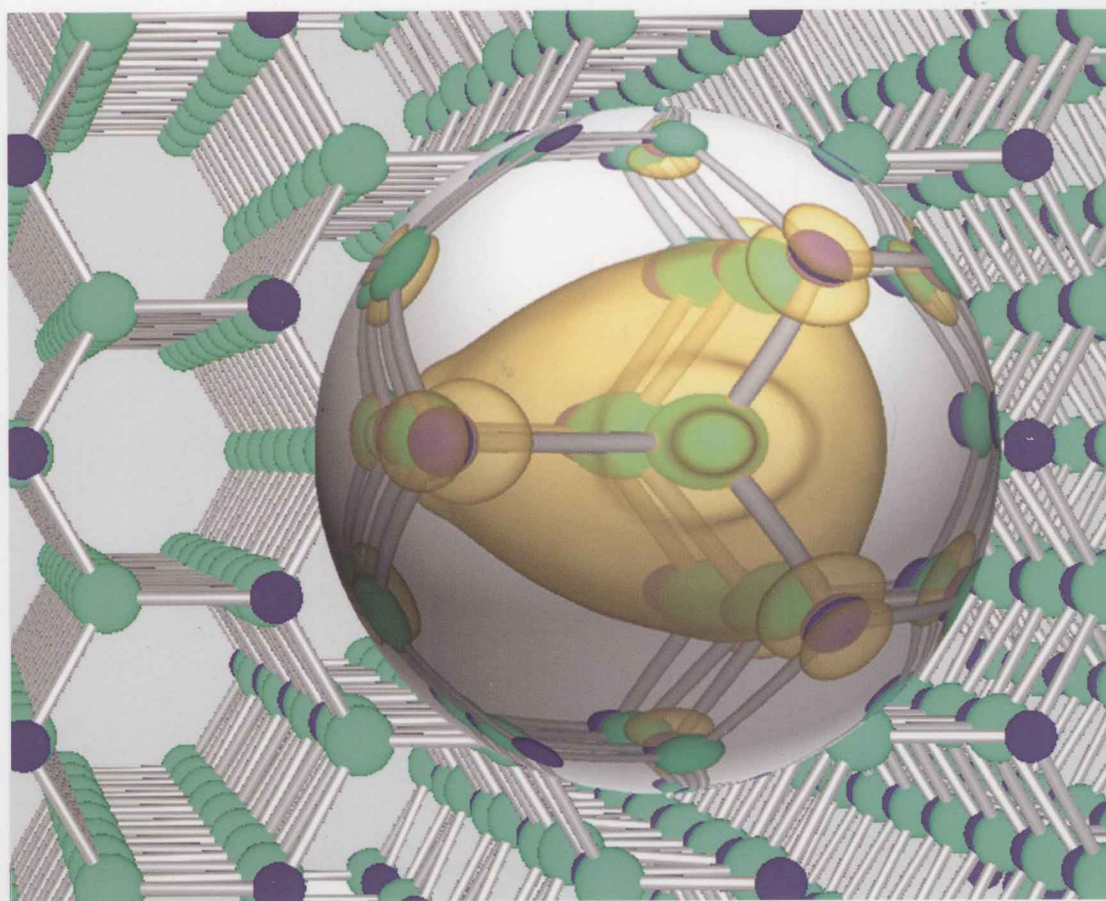


A. Alkauskas, P. Deák, J. Neugebauer,
A. Pasquarello, C. G. Van de Walle (Eds.)

WILEY-VCH

Advanced Calculations for Defects in Materials

Electronic Structure Methods



Edited by

*Audrius Alkauskas, Peter Deák, Jörg Neugebauer,
Alfredo Pasquarello, and Chris G. Van de Walle*

Advanced Calculations for Defects in Materials

Electronic Structure Methods



WILEY-VCH Verlag GmbH & Co. KGaA

The Editors

Dr. Audrius Alkauskas

EPFL 58, IPMC LSME
MX 136
Batiment MXC 12
1015 Lausanne
Schweiz

Prof. Dr. Peter Deák

Uni Bremen - Computational
Materials Science
Otto-Hahn-Allee 1
28359 Bremen

Prof. Dr. Jörg Neugebauer

Fritz-Haber-Institut
Max-Planck-Inst. f. Eisenfor.
Max-Planck-Str. 1
40237 Düsseldorf

Prof. Dr. Alfredo Pasquarello

EPFL-SB-ITP-CSEA
Station 3/ PH H2 467
1015 Lausanne
Schweiz

Prof. Dr. C. G. Van de Walle

Materials Department
University of California
Santa Barbara, CA 93106-5050
USA

All books published by **Wiley-VCH** are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

**Bibliographic information published by
the Deutsche Nationalbibliothek**

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

© 2011 Wiley-VCH Verlag & Co. KGaA,
Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Composition Thomson Digital, Noida, India

Printing and Binding Strauss GmbH, Mörlenbach

Cover Design Adam-Design, Weinheim

Printed in the Federal Republic of Germany

Printed on acid-free paper

ISBN: 978-3-527-41024-8

Edited by
Audrius Alkauskas, Peter Deák,
Jörg Neugebauer,
Alfredo Pasquarello, and
Chris G. Van de Walle

**Advanced Calculations for
Defects in Materials**

Related Titles

Brillson, L. J.

Surfaces and Interfaces of Electronic Materials

2010

ISBN: 978-3-527-40915-0

Magnasco, V.

Methods of Molecular Quantum Mechanics

An Introduction to Electronic Molecular Structure

2009

ISBN: 978-0-470-68442-9

Friedrichs, P., Kimoto, T., Ley, L., Pensl, G. (eds.)

Silicon Carbide

Volume 1: Growth, Defects, and Novel Applications

2010

ISBN: 978-3-527-40953-2

Friedrichs, P., Kimoto, T., Ley, L., Pensl, G. (eds.)

Silicon Carbide

Volume 2: Power Devices and Sensors

2010

ISBN: 978-3-527-40997-6

Sholl, D., Steckel, J. A

Density Functional Theory

A Practical Introduction

2009

ISBN: 978-0-470-37317-0

Tilley, R. J. D.

Defects in Solids

2008

ISBN: 978-0-470-07794-8

Morkoc, H.

Handbook of Nitride Semiconductors and Devices

2008

ISBN: 978-3-527-40797-2

List of Contributors

Audrius Alkauskas

Ecole Polytechnique Fédérale de
Lausanne (EPFL)
Institute of Theoretical Physics
1015 Lausanne
Switzerland

and

Institut Romand de Recherche
Numérique en Physique des Matériaux
(IRRMA)
1015 Lausanne
Switzerland

Bálint Aradi

Universität Bremen
Bremen Center for Computational
Materials Science
Am Fallturm 1
28359 Bremen
Germany

Stefano Baroni

CNR-IOM DEMOCRITOS
Theory@Elettra Group
s.s. 14 km 163.5 in Area Science Park
34149 Basovizza (Trieste)
Italy

and

SISSA – Scuola Internazionale
Superiore di Studi Avanzati
via Bonomea 265
34126 Trieste
Italy

Adisak Boonchun

Case Western Reserve University
Department of Physics
10900 Euclid Avenue
Cleveland, OH 444106-7079
USA

Patrick R. Briddon

Newcastle University
School of Electrical, Electronic and
Computer Engineering
Newcastle NE1 7RU
UK

Peter Broqvist

Ecole Polytechnique Fédérale de
Lausanne (EPFL)
Institute of Theoretical Physics
1015 Lausanne
Switzerland

and

Institut Romand de Recherche
Numérique en Physique des Matériaux
(IRRMA)
1015 Lausanne
Switzerland

Fabien Bruneval

European Theoretical Spectroscopy
Facility (ETSF)

and

CEA, DEN, Service de Recherches de
Métallurgie Physique
91191 Gif-sur-Yvette
France

G. Bussi

Universita di Modena e Reggio Emilia
CNR-NANO, S3 and Dipartimento di
Fisica
via Campi 213/A
41100 Modena
Italy

and

CNR-IOM Democritos and SISSA
via Bonomea 265
34136 Trieste
Italy

Marilia J. Caldas

Universidade de São Paulo
Instituto de Física
05508-900 São Paulo, SP
Brazil

S. J. Clark

Durham University
Physics Department
Durham
UK

Peter Deák

Universität Bremen
Bremen Center for Computational
Materials Science
Am Fallturm 1
28359 Bremen
Germany

Thomas Frauenheim

Universität Bremen
Bremen Center for Computational
Materials Science
Aon Fallturon
28359 Bremen
Germany

Christoph Freysoldt

Max-Planck-Institut für Eisenforschung
GmbH
Max-Planck-Str. 1
40237 Düsseldorf
Germany

Adam Gali

Hungarian Academy of Sciences
Research Institute for Solid State
Physics and Optics
POB 49
1525 Budapest
Hungary

and

Budapest University of Technology and
Economics
Department of Atomic Physics
Budafoki út 8
1111 Budapest
Hungary

Uwe Gerstmann

Universität Paderborn
Lehrstuhl für Theoretische Physik
Warburger Str. 100
33098 Paderborn
Germany

and

Université Pierre et Marie Curie
Institut de Minéralogie et de Physique
des Milieux Condensés
Campus Boucicaut
140 rue de Lourmel
75015 Paris
France

Luigi Giacomazzi

CNR-IOM DEMOCRITOS
Theory@Elettra Group
s.s. 14 km 163.5 in Area Science Park
34149 Basovizza (Trieste)
Italy

and

SISSA – Scuola Internazionale
Superiore di Studi Avanzati
via Bonomea 265
34126 Trieste
Italy

Matteo Giantomassi

European Theoretical Spectroscopy
Facility (ETSF)

and

Université catholique de Louvain
Institute of Condensed Matter and
Nanosciences
1 Place Croix du Sud, 1 bte 3
1348 Louvain-la-Neuve
Belgium

Blazej Grabowski

Max-Planck-Institut für Eisenforschung
GmbH
Max-Planck-Str. 1
40237 Düsseldorf
Germany

Myrta Grüning

European Theoretical Spectroscopy
Facility (ETSF)

and

University of Coimbra
Centre for Computational Physics and
Physics Department
Rua Larga
3004-516 Coimbra
Portugal

Thomas M. Henderson

Rice University
Departments of Chemistry and
Department of Physics and Astronomy
Houston, TX 77005
USA

Richard G. Hennig

Cornell University
Department of Materials Science and
Engineering
126 Bard Hall
Ithaca, NY 14853-1501
USA

Tilman Hickel

Max-Planck-Institut für Eisenforschung
GmbH
Max-Planck-Str. 1
40237 Düsseldorf
Germany

Anderson Janotti

University of California
Materials Department
Santa Barbara, CA 93106-5050
USA

Walter R. L. Lambrecht

Case Western Reserve University
Department of Physics
10900 Euclid Avenue
Cleveland, OH 44106-7079
USA

Stephan Lany

National Renewable Energy Laboratory
1617 Cole Blvd
Golden, CO 80401
USA

L. Martin-Samos

Universita di Modena e Reggio Emilia
CNR-NANO, S3 and Dipartimento di
Fisica
via Campi 213/A
41100 Modena
Italy

and

CNR-IOM Democritos and SISSA
via Bonomea 265
34136 Trieste
Italy

Nicola Marzari

Massachusetts Institute of Technology
Department of Materials Science and
Engineering
77 Massachusetts Avenue
Cambridge, MA 02139
USA

E. Molinari

Universita di Modena e Reggio Emilia
CNR-NANO, S3 and Dipartimento di
Fisica
via Campi 213/A
41100 Modena
Italy

Jörg Neugebauer

Max-Planck-Institut für Eisenforschung
GmbH
Max-Planck-Str. 1
40237 Düsseldorf
Germany

Joachim Paier

Rice University
Departments of Chemistry and
Department of Physics and Astronomy
Houston, TX 77005
USA

Present affiliation:

Humboldt-Universität
Zu Berlin
Institut für Chemie
Unter den Linden 6
10099 Berlin
Germany

William D. Parker

The Ohio State University
Department of Physics
191 W. Woodruff Ave.
Columbus, OH 43210
USA

Alfredo Pasquarello

Ecole Polytechnique Fédérale de
Lausanne (EPFL)
Institute of Theoretical Physics
1015 Lausanne
Switzerland

and

Institut Romand de Recherche
Numérique en Physique des Matériaux
(IRRMA)
1015 Lausanne
Switzerland

Xiaofeng Qian

Massachusetts Institute of Technology
Department of Materials Science and
Engineering
77 Massachusetts Avenue
Cambridge, MA 02139
USA

Mark J. Rayson

Max-Planck-Institut für Eisenforschung
GmbH
Max-Planck-Str. 1
40237 Düsseldorf
Germany

and

Luleå University of Technology
Department of Mathematics
97187 Luleå
Sweden

Gian-Marco Rignanese

European Theoretical Spectroscopy
Facility (ETSF)

and

Université catholique de Louvain
Institute of Condensed Matter and
Nanosciences
1 Place Croix du Sud, 1 bte 3
1348 Louvain-la-Neuve
Belgium

Patrick Rinke

European Theoretical Spectroscopy
Facility (ETSF)

and

University of California
Department of Materials
Santa Barbara, CA 93106-5050
USA

John Robertson

Cambridge University
Engineering Department
Cambridge CB2 1PZ
UK

A. Ruini

Università di Modena e Reggio Emilia
CNR-NANO, S3 and Dipartimento di
Fisica
via Campi 213/A
41100 Modena
Italy

Gustavo E. Scuseria

Rice University
Departments of Chemistry and Physics
and Astronomy
Houston, TX 77005
USA

Riad Shaltaf

European Theoretical Spectroscopy
Facility (ETSF)

and

University of Jordan
Department of Physics
Amman 11942
Jordan

Martin Stankovski

European Theoretical Spectroscopy
Facility (ETSF)

and

Université catholique de Louvain
Institute of Condensed Matter and
Nanosciences
1 Place Croix du Sud, 1 bte 3
1348 Louvain-la-Neuve
Belgium

Geoffroy Stenuit

CNR-IOM DEMOCRITOS
Theory@Elettra Group
s.s. 14 km 163.5 in Area Science Park
34149 Basovizza (Trieste)
Italy

Paolo Umari

CNR-IOM DEMOCRITOS
Theory@Elettra Group
s.s. 14 km 163.5 in Area Science Park
34149 Basovizza (Trieste)
Italy

Chris G. Van de Walle

University of California
Materials Department
Santa Barbara, CA 93106-5050
USA

Su-Huai Wei

National Renewable Energy Laboratory
1617 Cole Blvd
Golden, CO 80401
USA

John W. Wilkins

The Ohio State University
Department of Physics
191 W. Woodruff Ave.
Columbus, OH 43210
USA

Yanfa Yan

National Renewable Energy Laboratory
1617 Cole Blvd
Golden, CO 80401
USA

Contents

List of Contributors XIII

1	Advances in Electronic Structure Methods for Defects and Impurities in Solids	1
	<i>Chris G. Van de Walle and Anderson Janotti</i>	
1.1	Introduction	1
1.2	Formalism and Computational Approach	3
1.2.1	Defect Formation Energies and Concentrations	3
1.2.2	Transition Levels or Ionization Energies	4
1.2.3	Practical Aspects	5
1.3	The DFT-LDA/GGA Band-Gap Problem and Possible Approaches to Overcome It	6
1.3.1	LDA+U for Materials with Semicore States	6
1.3.2	Hybrid Functionals	9
1.3.3	Many-Body Perturbation Theory in the GW Approximation	12
1.3.4	Modified Pseudopotentials	12
1.4	Summary	13
	References	14
2	Accuracy of Quantum Monte Carlo Methods for Point Defects in Solids	17
	<i>William D. Parker, John W. Wilkins, and Richard G. Hennig</i>	
2.1	Introduction	17
2.2	Quantum Monte Carlo Method	18
2.2.1	Controlled Approximations	20
2.2.1.1	Time Step	20
2.2.1.2	Configuration Population	20
2.2.1.3	Basis Set	20
2.2.1.4	Simulation Cell	21
2.2.2	Uncontrolled Approximations	22
2.2.2.1	Fixed-Node Approximation	22

2.2.2.2	Pseudopotential	22
2.2.2.3	Pseudopotential Locality	23
2.3	Review of Previous DMC Defect Calculations	23
2.3.1	Diamond Vacancy	23
2.3.2	MgO Schottky Defect	25
2.3.3	Si Interstitial Defects	25
2.4	Results	25
2.4.1	Time Step	26
2.4.2	Pseudopotential	26
2.4.3	Fixed-Node Approximation	26
2.5	Conclusion	29
	References	29

3 **Electronic Properties of Interfaces and Defects from Many-body Perturbation Theory: Recent Developments and Applications** 33

Matteo Giantomassi, Martin Stankovski, Riad Shaltaf, Myrta Grüning, Fabien Bruneval, Patrick Rinke, and Gian-Marco Rignanese

3.1	Introduction	33
3.2	Many-Body Perturbation Theory	34
3.2.1	Hedin's Equations	34
3.2.2	GW Approximation	36
3.2.3	Beyond the GW Approximation	37
3.3	Practical Implementation of GW and Recent Developments Beyond	38
3.3.1	Perturbative Approach	38
3.3.2	QP Self-Consistent GW	40
3.3.3	Plasmon Pole Models <i>Versus</i> Direct Calculation of the Frequency Integral	41
3.3.4	The Extrapolar Method	44
3.3.4.1	Polarizability with a Limited Number of Empty States	45
3.3.4.2	Self-Energy with a Limited Number of Empty States	46
3.3.5	MBPT in the PAW Framework	46
3.4	QP Corrections to the BOs at Interfaces	48
3.5	QP Corrections for Defects	54
3.6	Conclusions and Prospects	57
	References	58

4 **Accelerating GW Calculations with Optimal Polarizability Basis** 61

Paolo Umari, Xiaofeng Qian, Nicola Marzari, Geoffrey Stenuit, Luigi Giacomazzi, and Stefano Baroni

4.1	Introduction	61
4.2	The GW Approximation	62
4.3	The Method: Optimal Polarizability Basis	64
4.4	Implementation and Validation	68
4.4.1	Benzene	69

4.4.2	Bulk Si	70
4.4.3	Vitreous Silica	70
4.5	Example: Point Defects in α - Si_3N_4	72
4.5.1	Model Generation	72
4.5.2	Model Structure	73
4.5.3	Electronic Structure	74
4.6	Conclusions	77
	References	77
5	Calculation of Semiconductor Band Structures and Defects by the Screened Exchange Density Functional	79
	<i>S. J. Clark and John Robertson</i>	
5.1	Introduction	79
5.2	Screened Exchange Functional	80
5.3	Bulk Band Structures and Defects	82
5.3.1	Band Structure of ZnO	83
5.3.2	Defects of ZnO	85
5.3.3	Band Structure of MgO	89
5.3.4	Band Structures of SnO_2 and CdO	90
5.3.5	Band Structure and Defects of HfO_2	91
5.3.6	BiFeO_3	92
5.4	Summary	93
	References	94
6	Accurate Treatment of Solids with the HSE Screened Hybrid	97
	<i>Thomas M. Henderson, Joachim Paier, and Gustavo E. Scuseria</i>	
6.1	Introduction and Basics of Density Functional Theory	97
6.2	Band Gaps	100
6.3	Screened Exchange	103
6.4	Applications	104
6.5	Conclusions	107
	References	108
7	Defect Levels Through Hybrid Density Functionals: Insights and Applications	111
	<i>Audrius Alkauskas, Peter Broqvist, and Alfredo Pasquarello</i>	
7.1	Introduction	111
7.2	Computational Toolbox	112
7.2.1	Defect Formation Energies and Charge Transition Levels	113
7.2.2	Hybrid Density Functionals	114
7.2.2.1	Integrable Divergence	115
7.3	General Results from Hybrid Functional Calculations	117
7.3.1	Alignment of Bulk Band Structures	118
7.3.2	Alignment of Defect Levels	120

7.3.3	Effect of Alignment on Defect Formation Energies	122
7.3.4	“The Band-Edge Problem”	124
7.4	Hybrid Functionals with Empirically Adjusted Parameters	125
7.5	Representative Case Studies	129
7.5.1	Si Dangling Bond	129
7.5.2	Charge State of O ₂ During Silicon Oxidation	131
7.6	Conclusion	132
	References	134
8	Accurate Gap Levels and Their Role in the Reliability of Other Calculated Defect Properties	139
	<i>Peter Deák, Adam Gali, Bálint Aradi, and Thomas Frauenheim</i>	
8.1	Introduction	139
8.2	Empirical Correction Schemes for the KS Levels	141
8.3	The Role of the Gap Level Positions in the Relative Energies of Various Defect Configurations	143
8.4	Correction of the Total Energy Based on the Corrected Gap Level Positions	146
8.5	Accurate Gap Levels and Total Energy Differences by Screened Hybrid Functionals	148
8.6	Summary	151
	References	152
9	LDA + <i>U</i> and Hybrid Functional Calculations for Defects in ZnO, SnO₂, and TiO₂	155
	<i>Anderson Janotti and Chris G. Van de Walle</i>	
9.1	Introduction	155
9.2	Methods	156
9.2.1	ZnO	158
9.2.2	SnO ₂	160
9.2.3	TiO ₂	161
9.3	Summary	163
	References	163
10	Critical Evaluation of the LDA + <i>U</i> Approach for Band Gap Corrections in Point Defect Calculations: The Oxygen Vacancy in ZnO Case Study	165
	<i>Adisak Boonchun and Walter R. L. Lambrecht</i>	
10.1	Introduction	165
10.2	LDA + <i>U</i> Basics	166
10.3	LDA + <i>U</i> Band Structures Compared to GW	168
10.4	Improved LDA + <i>U</i> Model	170
10.5	Finite Size Corrections	172
10.6	The Alignment Issue	173

10.7	Results for New LDA + U	174
10.8	Comparison with Other Results	176
10.9	Discussion of Experimental Results	178
10.10	Conclusions	179
	References	180
11	Predicting Polaronic Defect States by Means of Generalized Koopmans Density Functional Calculations	183
	<i>Stephan Lany</i>	
11.1	Introduction	183
11.2	The Generalized Koopmans Condition	185
11.3	Adjusting the Koopmans Condition using Parameterized On-Site Functionals	187
11.4	Koopmans Behavior in Hybrid-functionals: The Nitrogen Acceptor in ZnO	189
11.5	The Balance Between Localization and Delocalization	193
11.6	Conclusions	196
	References	197
12	SiO₂ in Density Functional Theory and Beyond	201
	<i>L. Martin-Samos, G. Bussi, A. Ruini, E. Molinari, and M.J. Caldas</i>	
12.1	Introduction	201
12.2	The Band Gap Problem	202
12.3	Which Gap?	204
12.4	Deep Defect States	207
12.5	Conclusions	209
	References	210
13	Overcoming Bipolar Doping Difficulty in Wide Gap Semiconductors	213
	<i>Su-Huai Wei and Yanfa Yan</i>	
13.1	Introduction	213
13.2	Method of Calculation	214
13.3	Symmetry and Occupation of Defect Levels	217
13.4	Origins of Doping Difficulty and the Doping Limit Rule	218
13.5	Approaches to Overcome the Doping Limit	220
13.5.1	Optimization of Chemical Potentials	220
13.5.1.1	Chemical Potential of Host Elements	220
13.5.1.2	Chemical Potential of Dopant Sources	222
13.5.2	H-Assisted Doping	223
13.5.3	Surfactant Enhanced Doping	224
13.5.4	Appropriate Selection of Dopants	226
13.5.5	Reduction of Transition Energy Levels	229
13.5.6	Universal Approaches Through Impurity-Band Doping	232

13.6	Summary	237
	References	238
14	Electrostatic Interactions between Charged Defects in Supercells	241
	<i>Christoph Freysoldt, Jörg Neugebauer, and Chris G. Van de Walle</i>	
14.1	Introduction	241
14.2	Electrostatics in Real Materials	243
14.2.1	Potential-based Formulation of Electrostatics	245
14.2.2	Derivation of the Correction Scheme	246
14.2.3	Dielectric Constants	249
14.3	Practical Examples	250
14.3.1	Ga Vacancy in GaAs	250
14.3.2	Vacancy in Diamond	252
14.4	Conclusions	254
	References	257
15	Formation Energies of Point Defects at Finite Temperatures	259
	<i>Blazej Grabowski, Tilmann Hickel, and Jörg Neugebauer</i>	
15.1	Introduction	259
15.2	Methodology	261
15.2.1	Analysis of Approaches to Correct for the Spurious Elastic Interaction in a Supercell Approach	261
15.2.1.1	The Volume Optimized Aapproach to Point Defect Properties	262
15.2.1.2	Derivation of the Constant Pressure and Rescaled Volume Approach	264
15.2.2	Electronic, Quasiharmonic, and Anharmonic Contributions to the Formation Free Energy	266
15.2.2.1	Free Energy Born–Oppenheimer Approximation	266
15.2.2.2	Electronic Excitations	269
15.2.2.3	Quasiharmonic Atomic Excitations	271
15.2.2.4	Anharmonic Atomic Excitations: Thermodynamic Integration	272
15.2.2.5	Anharmonic Atomic Excitations: Beyond the Thermodynamic Integration	274
15.3	Results: Electronic, Quasiharmonic, and Anharmonic Excitations in Vacancy Properties	278
15.4	Conclusions	282
	References	282
16	Accurate Kohn–Sham DFT With the Speed of Tight Binding: Current Techniques and Future Directions in Materials Modelling	285
	<i>Patrick R. Briddon and Mark J. Rayson</i>	
16.1	Introduction	285